

TRANSLATION FROM JAPANESE

- (19) JAPANESE PATENT OFFICE (JP)
(12) Unexamined Patent Gazette (A)
(11) Unexamined Patent Application (Kokai) No. 7-262984
(43) Disclosure Date: October 13, 1995

(51) Int. Cl. ⁶	Class. Symbols	Internal Office Registr. Nos.	F I	Technical Classification Field
H 01 M 4/02 4/58 10/40		C		
		Z		

Request for Examination: Not yet submitted
(Total of 7 pages [in original])

Number of Claims: 10 OL

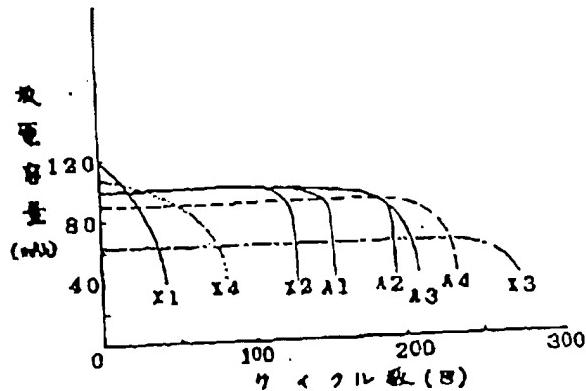
- (21) Application No.: 6-52053
(22) Filing Date: March 23, 1994
(71) Applicant: 000001889 (Sanyo Electric Co., Ltd.)
(72) Inventor: Yuji Yamamoto
(72) Inventor: Yoshihiro Shoji
(72) Inventor: Koji Nishio
(72) Inventor: Toshihiko Saito
(74) Agent: Satoshi Okada, Patent Attorney

(54) [Title of the Invention] Nonaqueous Electrolyte Secondary Cell

(57) [Summary]

[Composition] A mixture containing a lithium compound and LiMn₂O₄ is obtained, the mixture is then heat-treated at a temperature of 400–1325°C to produce a positive electrode active material, and the product is used to construct a nonaqueous electrolyte secondary cell.

[Merits] It is possible to obtain a nonaqueous electrolyte cell with improved cycle characteristics and consistently high discharge capacity.



[Key to figure: Discharge capacity (mAh), number of cycles (dimensionless units)]

[Claims]

[Claim 1] A nonaqueous electrolyte secondary cell, comprising a negative electrode in which lithium is used as the active material, a nonaqueous electrolyte, and a positive electrode whose positive electrode active material is a complex comprising Li_2MnO_3 and a lithium-manganese oxide having a spinel structure, wherein said nonaqueous electrolyte secondary cell is characterized in that the complex comprising Li_2MnO_3 and a lithium-manganese oxide having a spinel structure is obtained by heat-treating a mixture of a lithium compound and LiMn_2O_4 at a temperature of 400–1325°C.

[Claim 2] A nonaqueous electrolyte secondary cell as defined in Claim 1, characterized in that the mixture is heat-treated at a temperature of 850–950°C.

[Claim 3] A nonaqueous electrolyte secondary cell as defined in Claim 1, characterized in that the mixing ratio of the lithium compound and LiMn_2O_4 is 0.02–0.70 when expressed as the Li/Mn atomic ratio of the lithium in the lithium compound and the manganese in LiMn_2O_4 .

[Claim 4] A nonaqueous electrolyte secondary cell as defined in Claim 1, characterized in that the complex comprising Li_2MnO_3 and a lithium-manganese oxide having a spinel structure has an overall Li/Mn atomic ratio of 0.52–1.20 before being subjected to the electrochemical extraction and introduction of lithium.

[Claim 5] A nonaqueous electrolyte secondary cell as defined in Claim 1, characterized in that the lithium compound is lithium hydroxide.

[Claim 6] A method for manufacturing a nonaqueous electrolyte secondary cell, characterized in that a mixture of a lithium compound and LiMn_2O_4 is obtained, and this mixture is then heat-treated at a temperature of 400–1325°C.

[Claim 7] A method for manufacturing a nonaqueous electrolyte secondary cell as defined in Claim 6, characterized in that the mixture is heat-treated at a temperature of 850–950°C.

[Claim 8] A method for manufacturing a nonaqueous electrolyte secondary cell as defined in Claim 6, characterized in that the mixing ratio of the lithium compound and LiMn_2O_4 is 0.02–0.70 when expressed as the Li/Mn atomic ratio of the lithium in the lithium compound and the manganese in LiMn_2O_4 .

[Claim 9] A method for manufacturing a nonaqueous electrolyte secondary cell as defined in Claim 6, characterized in that a complex comprising Li_2MnO_3 and a lithium-manganese oxide having a spinel structure is obtained, and the overall Li/Mn atomic ratio of the complex is set to 0.52–1.20.

[Claim 10] A method for manufacturing a nonaqueous electrolyte secondary cell as defined in Claim 6, characterized in that the lithium compound is lithium hydroxide.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a nonaqueous electrolyte secondary cell whose positive electrode active material is a manganese oxide, and more particularly to an improvement for a positive electrode active material designed to obtain improved charge/discharge cycle characteristics.

[0002]

[Prior Art] Lithium-manganese oxides (LiMn_2O_4) having spinel structures, that is, lithium-manganese oxides expressed by the general formula $\text{Li}_{1-X}\text{Mn}_2\text{O}_4$ ($0 \leq X \leq 1$) such as the one disclosed in JP (Kokoku) 4-30146, have been an object of past research because such oxides yield high voltage when used as the positive electrode active materials of nonaqueous electrolyte secondary cells. A disadvantage of such lithium-manganese oxides with spinel structures is that they cannot be endowed with adequate cycle characteristics because manganese dissolves when the positive electrode is charged to a high potential.

[0003] Striving to overcome this disadvantage, the present inventors have previously proposed in their JP Patent Application (Tokugan) 4-280469 to form an Li_2MnO_3 layer on the surface of a particulate lithium-manganese oxide ($\text{Li}_{1-X}\text{Mn}_2\text{O}_4$; $0 \leq X \leq 1$) having a spinel structure and to obtain better cycle characteristics by mixing a lithium-manganese oxide (LiMn_2O_4) having a spinel structure with lithium hydroxide (LiOH), and heat-treating the mixture at 357°C. As can be seen in Fig. 3 of this application, increasing the ratio in which lithium hydroxide is admixed does indeed improve cycle characteristics, but a new problem of reduced discharge capacity is created.

[0004]

[Problems Which the Invention Is Intended to Solve] As a result of research conducted in view of the above-described situation, the inventors discovered that cell characteristics

could be changed by varying the heat treatment temperature of a mixture comprising lithium hydroxide and a lithium-manganese oxide having a spinel structure. Specifically, cycle characteristics can be further improved by setting a specific temperature range for the heat treatment of the mixture. It is also possible to improve the cycle characteristics while maintaining high discharge capacity.

[0005]

[Means Used to Solve the Above-Mentioned Problems] The present invention resides in a nonaqueous electrolyte secondary cell comprising a negative electrode in which lithium is used as the active material, a nonaqueous electrolyte, and a positive electrode whose positive electrode active material is a complex comprising Li_2MnO_3 and a lithium-manganese oxide having a spinel structure, wherein the cell is characterized in that the complex is obtained by heat-treating a mixture of a lithium compound and LiMn_2O_4 at a temperature of 400–1325°C.

[0006] The method for manufacturing a nonaqueous electrolyte secondary cell in accordance with the present invention is characterized in that a mixture of a lithium compound and LiMn_2O_4 is obtained, and this mixture is then heat-treated at a temperature of 400–1325°C.

[0007] In particular, heat-treating the mixture at a temperature of 850–950°C is preferred from the standpoint of cycle characteristics and discharge capacity.

[0008] The mixing ratio of the lithium compound and LiMn_2O_4 should be set to 0.02–0.70 when expressed as the Li/Mn atomic ratio of the lithium in the lithium compound and the manganese in LiMn_2O_4 .

[0009] Another distinctive feature is that the complex comprising Li_2MnO_3 and a lithium-manganese oxide having a spinel structure has an overall Li/Mn atomic ratio of 0.52–1.20 before being subjected to the electrochemical extraction and introduction of lithium.

[0010] Examples of lithium compounds that can be mixed with LiMn_2O_4 and heat-treated as described above include, in addition to lithium hydroxide (LiOH), compounds such as hydrated lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$), lithium carbonate (Li_2CO_3), lithium oxide (Li_2O), and lithium nitrate (LiNO_3). In particular, using lithium hydroxide (LiOH) is beneficial because lithium hydroxide is readily available, remains stable during such manufacturing processes, and has high reactivity during a heat treatment. In addition,

LiMn_2O_4 , which is a secondary starting material for the positive electrode active material, can be readily synthesized and is not limited in any particular way in terms of synthesis techniques.

[0011] Examples of solvents that can be used to obtain the cell of the present invention include propylene carbonate (PC), ethylene carbonate (EC), butylene carbonate (BC), vinyl carbonate (VC), γ -butyrolactone (γ -BL), dimethyl carbonate (DMC), diethyl carbonate (DEC), methylethyl carbonate (MEC), dimethoxyethane (DME), tetrahydrofuran (THF), dioxolane (DOXL), and 1,2-diethoxyethane (DEE). Mixtures of these can be appropriately used in accordance with the desired cell design.

[0012] Examples of suitable solutes include LiCF_3SO_3 , LiBF_4 , LiAsF_6 , and LiClO_4 , of which LiPF_6 and LiCF_3SO_3 are particularly preferred because of considerations related to the characteristics of secondary cells.

[0013] A lithium alloy or a carbon material such as graphite may also be used for the negative electrode of such a cell in addition to lithium metal, which is a material capable of absorbing and releasing lithium as an active material.

[0014]

[Operation of the Invention] According to the present invention, the positive electrode active material is a complex compound configured such that an Li_2MnO_3 layer is formed on the particulate surface of a lithium-manganese oxide (LiMn_2O_4) having a spinel structure. A reduction can thus be achieved for the surface area of direct contact between the electrolyte and the LiMn_2O_4 in the positive electrode active material, suppressing the elution of Mn from the LiMn_2O_4 during charging. An X-ray diffraction analysis of the complex compound confirms that the diffraction peak on the high-angle side of the lithium-manganese oxide (LiMn_2O_4) having a spinel structure is shifted toward higher angles in comparison with a simple mixture of particulate Li_2MnO_3 and a particulate lithium-manganese oxide (LiMn_2O_4) having a spinel structure. This proves that the aforementioned complex compound has formed a complex rather than a simple mixture, and constitutes a distinctive feature of the inventive positive electrode active material.

[0015] The positive electrode active material is a complex of Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) whose crystal structure remains the same spinel structure as long as the heat treatment temperature is set to 375°C or 400°C. Setting the heat treatment temperature above 400°C causes the Li_2MnO_3 layer on the surface of the

particulate positive electrode active material to become more uniform and dense in the case of a complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure, and is thus believed to be more effective in protecting the lithium-manganese oxide (LiMn_2O_4) having the spinel structure inside the particles, and to act to improve cycle characteristics.

[0016] It was also confirmed that 1400°C is the maximum permissible heat treatment temperature in terms of acceptable cycle characteristics. This temperature cannot be considered desirable in terms of discharge capacity, however. This is probably due to the partial decomposition of the lithium-manganese oxide (LiMn_2O_4) having a spinel structure in the positive electrode active material. X-ray diffraction analyses of positive electrode active materials heat-treated at such high temperatures have revealed the presence of Mn_3O_4 , which is believed to be a decomposition product.

[0017] A cell obtained using a positive electrode active material heat-treated at a temperature of 1325°C has good cycle characteristics but possesses a somewhat diminished discharge capacity. This is believed to be due to the fact that the Li_2MnO_3 layer on the surface of the positive electrode active material is overdeveloped at this temperature, tending to impede the electrode reactions between the electrolyte and the lithium-manganese oxide (LiMn_2O_4) with a spinel structure in the particles of the active material. The upper level of the heat treatment should therefore be set to the aforementioned temperature.

[0018] A complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure can still be obtained when a lithium compound and a manganese compound are mixed in an Li/Mn atomic ratio of 0.5 or greater and baked at a temperature of about 500°C or greater. The complex thus obtained is configured such that its particles contain randomly distributed Li_2MnO_3 crystal layers and spinel crystal layers. Consequently, this structure differs from the structure targeted by the present invention, namely, a structure in which a lithium-manganese oxide (LiMn_2O_4) having a spinel structure is contained inside particles, and Li_2MnO_3 is selectively layered on the particle surfaces. The result is that because an Li_2MnO_3 layer is less effective in reducing the surface area of contact between an LiMn_2O_4 layer and an electrolyte, the arrangement described above is inferior to the one provided by the present invention in terms of obtaining improved cycle characteristics while maintaining high discharge capacity.

[0019]

[Working Examples] A description will now be given with reference to the working examples of the present invention.

(Working Example 1)

(Fabrication of Positive Electrode) A mixture was obtained by mixing lithium hydroxide (LiOH) and manganese dioxide as starting materials in an Li:Mn molar ratio of 1:2, and the mixture was baked for 20 hours in air at 850°C, yielding LiMn_2O_4 . The LiMn_2O_4 and lithium hydroxide (LiOH) were mixed in amounts of 1 and 0.2 mol, respectively, and the mixture was heat-treated for 20 hours in air at 400°C, yielding a complex. Expressed as the Li/Mn atomic ratio of the lithium in the lithium hydroxide (LiOH) and the manganese in LiMn_2O_4 , the corresponding mixing ratio was 0.1.

[0020] The resulting complex was measured by X-ray diffraction, the results were compared with those on a JSPDS card, the presence of diffraction lines was confirmed for LiMn_2O_4 and Li_2MnO_3 , and, in particular, the LiMn_2O_4 was found to have a spinel structure. The particulate structure of the complex was believed to consist of complex particles in which an Li_2MnO_3 layer was formed on the surface of the particulate lithium-manganese oxide (LiMn_2O_4) having a spinel structure. The overall Li/Mn atomic ratio of the complex comprising Li_2MnO_3 and the lithium-manganese oxide (LiMn_2O_4) having a spinel structure was also measured by atomic absorptiometry and found to be 0.60.

[0021] A positive electrode mix was obtained by mixing the following components in a weight ratio of 85/10/5: a positive electrode active material in the form of a complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure, carbon black as a conductive agent, and a fluororesin as a binder. The positive electrode mix was molded, and a discoid positive electrode was fabricated. The positive electrode was then dried for 20 hours in a vacuum at 250°C, and used in the manufacture of a cell.

[0022] (Fabrication of Negative Electrode) Lithium metal was rolled and punched, and a discoid negative electrode was fabricated. A stainless steel plate (SUS 304) was used for the negative electrode collector.

[0023] (Preparation of Nonaqueous Electrolyte) LiPF_6 (lithium hexafluorophosphate) was dissolved to a concentration of 1 mol/L in an equal-volume mixed solvent

comprising propylene carbonate (PC) and 1,2-dimethoxyethane (DME), and a nonaqueous electrolyte was prepared.

[0024] (Cell Assembly) Fig. 1 is a fragmentary cross-sectional view of a flat nonaqueous electrolyte cell pertaining to a working example of the present invention. In the drawing, 1 is a negative electrode composed of lithium metal and crimped onto a negative electrode collector 3 affixed to the internal bottom surface of a negative electrode jar 2. 4 is a positive electrode, which is an important feature of the present invention and which is compression-bonded to a positive electrode collector 6, itself affixed to the internal bottom surface of a positive electrode jar 5. Stainless steel plate (SUS 316) was used for the positive electrode jar 5 and positive electrode collector 6, and another type of stainless steel plate (SUS 304) was used for the negative electrode 1 and the negative electrode collector 3. 7 is a separator composed of a porous polypropylene membrane and impregnated with the nonaqueous electrolyte prepared in the above-described manner. 8 is an insulating packing. The cell had a diameter of 24 mm and a height of 3 mm, and constituted inventive cell A1.

(Working Example 2) Inventive cell A2 was fabricated in the same manner as in Working Example 1 above except that a mixture comprising LiMn₂O₄ and lithium hydroxide (LiOH) was heat-treated at a temperature of 850°C to fabricate a complex that served as a positive electrode active material and comprised Li₂MnO₃ and a lithium-manganese oxide (LiMn₂O₄) having a spinel structure.

(Working Example 3) Inventive cell A3 was fabricated in the same manner as in Working Example 1 above except that a mixture comprising LiMn₂O₄ and lithium hydroxide was heat-treated at a temperature of 950°C to fabricate a complex that served as a positive electrode active material and comprised Li₂MnO₃ and a lithium-manganese oxide having a spinel structure.

(Working Example 4) Inventive cell A4 was fabricated in the same manner as in Working Example 1 above except that a mixture comprising LiMn₂O₄ and lithium hydroxide was heat-treated at a temperature of 1350°C to fabricate a complex that served as a positive electrode active material and comprised Li₂MnO₃ and a lithium-manganese oxide having a spinel structure.

(Comparative Example 1) Comparison cell X1 was fabricated in the same manner as in Working Example 1 above except that a lithium-manganese oxide (LiMn_2O_4) having a spinel structure was used as the positive electrode active material.

(Comparative Example 2) Comparison cell X2 was fabricated in the same manner as in Working Example 1 above except that a mixture comprising LiMn_2O_4 and lithium hydroxide was heat-treated at a temperature of 375°C to fabricate a complex that served as a positive electrode active material and comprised Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure.

[0025] Comparison cell X2 is identical to the cell described in Working Example 1 of JP (Tokugan) 4-280469, as mentioned in the Prior Art section of the present specification.

(Comparative Example 3) Comparison cell X3 was fabricated in the same manner as in Working Example 1 above except that a mixture comprising LiMn_2O_4 and lithium hydroxide was heat-treated at a temperature of 1400°C to fabricate a complex that served as a positive electrode active material and comprised Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure.

(Comparative Example 4) Comparison cell X4 was fabricated in the same manner as in Working Example 1 above except that 0.6 mol of lithium hydroxide (LiOH) and 1 mol of manganese dioxide (MnO_2) were mixed and the resulting mixture was baked for 20 hours in air at 850°C to fabricate a complex that served as a positive electrode active material and comprised Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure.

[0026] Table 1 shows the active material mixing ratios, heat treatment temperatures, product Li/Mn ratios, and product crystal structures of the cells fabricated as described above with reference to Working Examples 1-4 and Comparative Examples 1-4.

[0027]
[Table 1]

	Mixing ratio of starting materials LiOH + LiMn ₂ O ₄ ; Li (in LiOH)/Mn (in LiMn ₂ O ₄)	Li compound + LiMn ₂ O ₄ ; heat treatment temperature (°C)	Li/Mn ratio of product	Crystal structure of product
Comparative Example 1	0	None	0	LiMn ₂ O ₄
Comparative Example 2	0.2	375	0.60	Li ₂ MnO ₃ + LiMn ₂ O ₄
Working Example 1	0.2	400	0.60	Li ₂ MnO ₃ + LiMn ₂ O ₄
Working Example 2	0.2	850	0.60	Li ₂ MnO ₃ + LiMn ₂ O ₄
Working Example 3	0.2	950	0.60	Li ₂ MnO ₃ + LiMn ₂ O ₄
Working Example 4	0.2	1325	0.60	Li ₂ MnO ₃ + LiMn ₂ O ₄
Comparative Example 3	0.2	1400	0.60	Li ₂ MnO ₃ + LiMn ₂ O ₄
Comparative Example 4	0.6	850 (LiOH + MnO ₂)	0.60	Li ₂ MnO ₃ + LiMn ₂ O ₄

[0028] (Cycle Tests) Inventive cells A1-A4 and comparison cells X1-X4 were subjected to cycle tests in which each cycle entailed charging the cells to 4.5 V at 3 mA under room temperature conditions (25°C) and then discharging the cells to 3.0 V at 3 mA. The cycle characteristics of each cells were then analyzed. The results are shown in Fig. 2. Fig. 2 shows the relation between the number of charge/discharge cycles (dimensionless units) and the discharge capacity (mAh) of inventive cells A1-A4 and comparison cells X1-X4.

[0029] It can be seen in Fig. 2 that comparison cell X2, in which a complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure is used as the positive electrode active material, has somewhat better cycle characteristics than does comparison cell X1, in which solely a lithium-manganese oxide (LiMn_2O_4) having a spinel structure is used as the positive electrode active material. This is believed to be due to the fact that the positive electrode active material is configured such that an Li_2MnO_3 layer covers the surface of the particulate lithium-manganese oxide (LiMn_2O_4) having a spinel structure, thus reducing the surface area of direct contact between the electrolyte and the lithium-manganese oxide with a spinel structure in the positive electrode active material, and suppressing the elution of manganese from the lithium-manganese oxide having a spinel structure during charging.

[0030] Inventive cell A1 has better cycle characteristics than does comparison cell X2. The positive electrode active materials used in the production of comparison cell X2 and inventive cell A1 have the same complex crystal structures, that is, a complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure, but comparison cell X2 was fabricated at 375°C while inventive cell A1 was fabricated at 400°C. Based on this fact, it is assumed that adopting a higher fabrication temperature for a complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure results in the formation of a more uniform and dense Li_2MnO_3 layer on the particulate surface of the positive electrode active material, providing enhanced action in terms of improving the cycle characteristics of the lithium-manganese oxide (LiMn_2O_4) with a spinel structure while protecting the LiMn_2O_4 inside the particles.

[0031] It is also possible to preserve the high discharge capacity and to further improve the cycle characteristics in the case of inventive cells A2 and A3, which were obtained by processes in which the fabrication temperature of the complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure was raised to 850°C and 950°C, respectively. The following reasons for this outcome can be offered.

Specifically, it is believed that a uniformly dense Li_2MnO_3 layer is formed in this temperature range on the particulate surface of the positive electrode active material in the form of a complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure, but the Li_2MnO_3 layer is adequately developed and does not impede electrode reactions between the electrolyte and the lithium-manganese oxide (LiMn_2O_4) with a spinel structure in the particles of the active material.

[0032] It should be noted, however, that adequate cycle characteristics but diminished discharge capacity are obtained when inventive cell A4 is produced by selecting 1325°C as the fabrication temperature of the complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure. This temperature is believed to create an excessively developed Li_2MnO_3 layer on the surface of the positive electrode active material and to impede electrode reactions between the electrolyte and the lithium-manganese oxide (LiMn_2O_4) with a spinel structure.

[0033] The discharge capacity is markedly reduced in the case of comparison cell X3, which was obtained by further raising the fabrication temperature of the complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure, and setting the heat treatment temperature to 1400°C. This is attributed to the decomposition of the lithium-manganese oxide (LiMn_2O_4) with a spinel structure in the positive electrode active material.

[0034] Comparison cell X4, which was fabricated by a process in which a complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure was heat-treated in a single step as a starting material, is similar to inventive cells A1 and A2 in that the complex has the same overall Li/Mn ratio, and the Li_2MnO_3 and LiMn_2O_4 phases are present in the same ratio. In this comparison cell, however, Li_2MnO_3 and LiMn_2O_4 phases are randomly distributed inside the particles, making it impossible to obtain a structure in which Li_2MnO_3 is selectively formed on the surfaces of the particles in the same manner as in the case of the positive electrode active material used in the production of inventive cells. Comparison cell X4 is therefore inferior to inventive cells A1-A4 in terms of cycle characteristics.

[0035] It follows from the above description that mixing and heat-treating LiMn_2O_4 and a lithium compound are necessary conditions for manufacturing a complex comprising Li_2MnO_3 and a lithium-manganese oxide (LiMn_2O_4) having a spinel structure. In addition, the fabrication temperature (that is, the heat treatment temperature) should be

kept between 400°C and 950°C because of considerations related to keeping the discharge capacity of the cell at a high level, and should be kept between 850°C and 1325°C because of considerations related to obtaining improved cycle characteristics. The temperature should therefore be kept between 850°C and 950°C when both the discharge capacity and cycle characteristics are taken into account.

[0036] In this case, mixing lithium hydroxide (LiOH) with LiMn₂O₄ in an excessively low ratio yields an Li₂MnO₃ surface layer that is rough and thin, making it impossible to adequately protect the internal LiMn₂O₄ or to improve characteristics. Mixing too much lithium hydroxide will yield more Li₂MnO₃ (which does not contribute to charge/discharge reactions) and reduce the discharge capacity of the product as a positive electrode active material. Consequently, the optimum mixing ratio falls within a range of 0.02–0.70 when expressed as the Li/Mn atomic ratio of the lithium in the lithium compound and the manganese in LiMn₂O₄ (starting material). The result, expressed as the overall Li/Mn atomic ratio of the complex product comprising Li₂MnO₃ and a lithium-manganese oxide (LiMn₂O₄) having a spinel structure, will be 0.52–1.20. In addition, LiMn₂O₄, which is a starting material for the positive electrode active material, can be readily synthesized and is not limited in any particular way in terms of synthesis techniques.

[0037]

[Merits of the Invention] As described above, the cycle characteristics of cells can be improved in accordance with the present invention. In addition, the cycle characteristics can be improved while high discharge capacity can be maintained, resulting in an extremely high commercial value.

[Brief Description of the Figures]

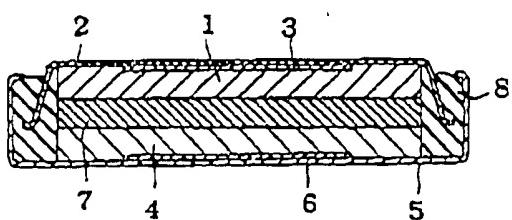
[Figure 1] A cross-sectional view of an inventive cell fabricated in accordance with a working example.

[Figure 2] A diagram depicting the relation between the number of cycles and the discharge capacity of inventive and comparison cells.

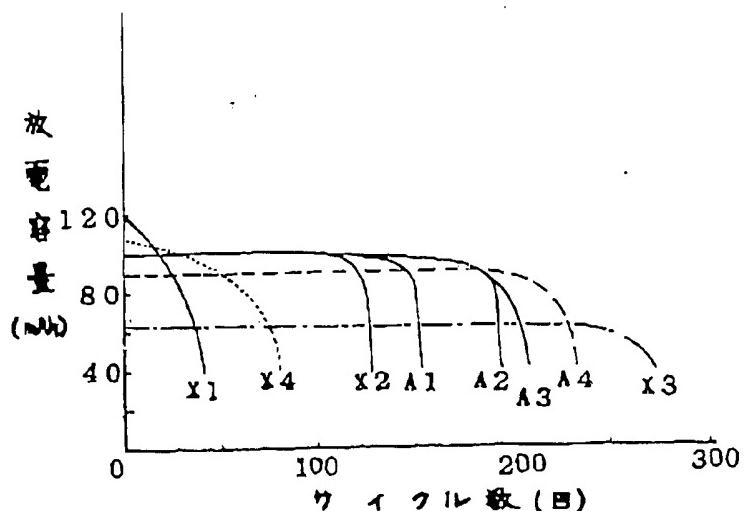
[Key]

1: negative electrode, 2: negative electrode jar, 3: negative electrode collector,
4: positive electrode, 5: positive electrode jar, 6: positive electrode collector, 7: separator,
8: insulating packing, A1–A4: inventive cells, X1–X4: comparison cells

[Figure 1]



[Figure 2]



[Key to figure: Discharge capacity (mAh), number of cycles (dimensionless units)]